

SUPPORTING INFORMATION

EARLY DIAGENESIS OF LACUSTRINE CARBONATES IN VOLCANIC SETTINGS: CHARACTERIZATION AND MODELING UNRAVELLING THE ROLE OF MAGMATIC GASES (LAKE DZIANI DZAHA, MAYOTTE, INDIAN OCEAN)

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Table S1. Cl and Br concentrations of the Dziani Dzaha water column above the 18 m depression collected in April 2015 and comparison with seawater.

Depth (m)*	Br (mM)**	Cl (mM)**	Cl/Br	$\Delta_{Cl/Br \text{ lake-Cl/Br sea water}} (\%)$	$Cl_{\text{lake}}/Cl_{\text{seawater}}$
3	1.33	923	694	6.7	1.69
4	1.35	943	696	7.1	1.73
5	1.36	948	697	7.2	1.74
7	1.35	944	699	7.5	1.73
9	1.37	953	698	7.4	1.75
11	1.36	948	699	7.6	1.74
13	1.36	953	703	8.1	1.74
seawater	0.84	546	650	-	-

*depths corresponding to the water column section below the pycnocline and above the monimolimnion (where the water does not intermix)

**measured with UV spectrophotometric

Table S2. Sediment cores, lake waters and bubbling gases sampled in the Dziani Dzaha

Sample	GPS coordinates (degree min)	
	Latitude South	Longitude East
<i>Sediment cores</i>		
DZ12-4 C1	S 12°46.269'	E 45°17.288'
DZ12-4 C2	S 12°46.269'	E 45°17.288'
DZ14-4 C4	S 12°46.223'	E 45°17.275'
DZ14-10 C6	S 12°46.235'	E 45°17.392'
DZ14-10 C10	S 12°46.169'	E 45°17.265'
DZ16-8 C12	S 12°46.245'	E 45°17.335'
<i>Water column</i>		
DZ10-9 WC		
DZ11-9 WC		
DZ12-4 WC	S 12°46.235'	E 45°17.392'
DZ14-4 WC		
DZ16-8 WC		
<i>Bubbling gas</i>		
DZ16-8 G2	S 12°46.232'	E 45°17.362'
DZ16-8 G3	S 12°46.167'	E 45°17.257'
DZ16-8 G4	S 12°46.250'	E 45°17.150'
DZ16-8 G5	S 12°46.253'	E 45°17.152'
DZ16-8 G7	S 12°48.013'	E 45°17.345'
DZ16-8 G10	S 12°46.250'	E 45°17.150'
DZ16-8 G11	S 12°46.311'	E 45°17.257'
DZ16-8 G12	S 12°46.321'	E 45°17.272'

Table S3. Concentration of dissolved methane and CO₂ in the water column straight up the 18 m depression (DZ14-4 WC). Standard deviation is $\pm 7\%$ of the measured value.

Depth (m)	CO ₂ (μM)	CH ₄ (μM)
1	24	91
5	168	1519
11	158	1714
16	266	3043
18	264	3180

Table S4. Carbon and hydrogen isotope compositions of dissolved CH₄ and carbon isotope composition of CO₂ in the pore waters of the sediment core C12. Standard deviation for carbon and hydrogen isotope composition is ±1‰ and ±5‰, respectively.

Depth (cm)	δ ¹³ C _{CH₄} (‰)	δD _{CH₄} (‰)	δ ¹³ C _{CO₂} (‰)
1	-63.2	-	2.3
9	-67.6	-230.2	2.7
21	-66.8	-	2.1
33	-	-	3.4
45	-71.3	-	4.6
61	-70.0	-177.4	4.9
73	-68.8	-	5.3
85	-66.5	-214.2	5.8
89	-68.5	-	5.8
105	-66.5	-209.5	6.6

Table S5. Porosity values in the sediment core C12

Depth (cm)	Porosity (%)
0 - 0.6	98.2
0.6 - 1.4	97.6
1.5 - 4	94.7
4 - 6.5	93.7
6.5 - 12	95.2
12.5 - 15.5	93.0
15.5 - 19	89.4
20 - 24	91.9
24 - 29	90.0
29 - 32.5	89.8
32.5 - 35	90.4
35 - 38	89.7
38 - 41	90.4
41 - 44	90.9
44 - 47	91.0
47 - 51	91.5
51 - 54.5	90.8
54.5 - 59	92.2
59 - 64	92.3
64 - 67	93.3
67 - 69.5	86.8
69.5 - 74	89.1
74 - 79	89.0
79 - 84.5	82.8
84.5 - 89	83.5
89 - 93	86.7
93 - 96	88.5
96 - 101.5	84.3
101.5 - 103.5	90.4

Table S6. pH, alkalinity and major cation concentrations measured in the pore waters of the sediment core C12. Relative standard deviation is $\leq 5\%$ for alkalinity and cation concentrations and ± 0.02 units for pH values.

Depth (cm)	pH	Alkalinity (mM)	Na (mM)	K (mM)	Mg (mM)	Ca (μ M)	Si (μ M)
0	8.98	225.1	939.0	33.1	3.8	56	170
3	8.86	-	981.5	35.3	3.4	128	162
7	8.85	236.6	1009.5	35.3	2.4	41	83
11	8.81	236.8	992.1	34.9	2.2	79	187
15	8.78	236.7	998.9	36.4	1.8	63	118
19	8.78	236.0	1037.6	37.9	1.7	40	175
23	8.89	233.6	1005.4	37.2	1.7	81	145
27	8.77	232.8	1009.9	37.1	1.7	76	88
31	8.77	230.1	1014.6	37.1	1.7	56	69
35	8.80	230.6	1003.6	36.8	1.7	76	87
39	8.75	226.6	1008.5	36.4	1.8	55	100
43	8.52	225.4	943.8	35.0	1.8	58	171
47	8.56	224.1	949.8	34.9	1.7	71	126
51	8.63	224.1	960.5	33.8	1.8	78	142
55	8.57	221.3	964.2	35.5	1.8	95	165
59	8.60	219.4	974.3	35.6	1.9	71	154
63	8.57	223.6	921.9	34.2	1.9	90	163
67	8.84	-	861.2	29.9	1.9	155	276
71	8.44	218.5	936.4	34.4	2.1	65	170
75	8.49	217.4	924.9	33.7	2.2	75	170
79	8.44	217.2	921.5	33.5	2.2	96	185
83	8.42	216.2	910.8	32.8	2.3	61	196
87	8.44	215.4	888.6	32.7	2.4	125	211
91	8.49	214.5	885.7	32.4	2.5	75	234
95	8.36	215.4	888.1	32.5	2.6	78	252
99	8.30	215.1	876.1	32.0	2.7	62	259
103	8.39	216.0	858.4	31.3	2.8	62	364

Section S1. Sensitivity tests and discrepancies between field and laboratory rates

Sensitivity tests have been performed on several parameters including the kinetic rate constant, the thermodynamic parameters, specific surface areas and the secondary phases involved in the reaction. Different values of rate and equilibrium constants of hydromagnesite were tested to address the discrepancy of hydromagnesite content and Mg concentration between the model and the observations. Increasing the rate constant decreases the hydromagnesite content at depth which is in better agreement with the data; however, it increases the Mg concentrations of the pore waters. Adopting the equilibrium constant of the MINTEQA2 database¹, 0.8 log unit lower than the one of the Thermoddem database^{2,3}, leads to similar result. The decrease of the diopside content with depth due to its dissolution requires the use of a specific surface area one order of magnitude higher than literature values. If a lower surface area is considered, the diopside content remains constant all along the sedimentary column. The surface area used for diopside is reasonable considering that the literature values range over orders of magnitude⁴. Alternatively, paleoenvironmental changes such as variations in the detrital inputs to the lake, could explain the observed decrease of the diopside content with depth. The suppression of microcline or saponite in the model, or the decrease of their rate constants results in an increase of silica concentrations

to values up to one order of magnitude higher than the measured concentrations. Those two phases are thus essential to explain the silica balance of the lake. The saponite used for the calculation is theoretical and does not have the actual stoichiometry of the saponite of the Dziani sediment⁵ (Table S7). The Si/Mg ratio in the theoretical formula is lower than in the measured one, such that more magnesium is needed to form saponite in the calculation than in the field. Thermodynamic constants were determined for the saponite of the Dziani Dzaha sediment (DZ-Saponite) (Table S7). Calculations were performed considering anhydrous phases, based on the theory of Blanc et al.³ (Section S2). Those authors provided a predictive model to determine the thermodynamic parameters (*i.e.*, enthalpy (ΔH), entropy (S) and heat capacity (Cp)) of anhydrous phyllosilicates. Despite their chemical and structural differences, the two phases have similar thermodynamic constants (Table S7 and Section S2).

The rate constant used for saponite ($10^{-18} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) is low compared to values from laboratory experiments on clay minerals⁶ but consistent with results from previous modeling studies⁷. Several factors can influence the rate constant of minerals and explain lower values in natural environment compared to laboratory experiments. Constant rates from laboratory experiments are usually determined on mineral powders with specific surface areas higher than the reactive surface areas found in natural conditions⁸⁻¹². In addition, most of the rate constants are determined in dissolution experiments and are usually considered to be equal for precipitation. However, as established for quartz¹³ or clays¹⁴, rate constants for precipitation are slower than for dissolution. Furthermore, the evolution of surface morphology with time is difficult to consider¹¹ and more importantly reaction sites will become less reactive while dissolution of phase will create new fresh surface. Finally, the presence of mineral precursors such as primary silicates can facilitate the nucleation of clay minerals¹⁵.

Table S7. Stoichiometry and equilibrium constants of dissolution reaction of saponite of the Thermoddem database² and of the Dziani sediment (DZ-saponite)⁵

Mineral	Chemical formula	Si/Mg	Log K								V _m (cm ³ mol ⁻¹)
			0°C	25°C	50°C	100°C	150°C	200°C	250°C	300°C	
Saponite(Mg)	Mg _{0.17} Mg ₃ Al _{0.34} Si _{3.66} O ₁₀ (OH) ₂	1.15	33.21	28.79	23.86	19.51	15.33	11.99	9.10	6.41	138.58
DZ-Saponite	K _{0.01} Mg _{0.12} Ca _{0.02} Na _{0.28} (Mg _{2.49} Al _{0.28}) (Si _{3.61} Al _{0.39})O ₁₀ (OH) ₂	1.38	33.45	28.84	23.69	19.15	14.86	11.64	6.91	5.45	140.42

The base components are: Al³⁺, Ca²⁺, H⁺, H₂O, Mg²⁺, K⁺, Na⁺ and H₄SiO₄.

Section S2. Thermodynamic constants of DZ-Saponite

The temperature dependence of the equilibrium constant (K_{eq}) was calculated considering the formula²:

$$\log_{10}(K_{eq}) = A + B.T + C.T^{-1} + D.\log_{10}(T) + E.T^{-2} \quad \text{Eqs (S1)}$$

with T the temperature in Kelvin and A , B , C , D and E the analytical parameters (Table S8). The analytical parameters of the DZ-saponite are close to those of the Thermoddem database². The enthalpy of reactions can also be used with the Van't Hoff approximation to calculate the equilibrium constant at high temperatures, but it is often less accurate.

Table S8. Analytical parameters of Eqs (S1) and enthalpy of reaction of the DZ-saponite

Phase	A	B	C	D	E	ΔH_r° (kJ·mol ⁻¹)
DZ-saponite	-108.68	0.00	18743.21	30.17	0.00	-284.656

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